

Chapter 3

BASICS OF CORROSION MEASUREMENTS

Mixed-Potential Theory. The mixed potential-theory (1) consists of two simple hypothesis: (1) any electrochemical reaction can be divided into two or more partial oxidation and reduction reactions and (2) there can be no net accumulation of electric charge during an electrochemical reaction.

It can be experimentally demonstrated that electrochemical reactions are composed of two or more partial oxidation or reduction reactions. The second hypothesis is a restatement of the law of conservation of charge. It follows that during the corrosion of an electrically isolated metal sample, the total rate of oxidation must equal the total of reduction.

Corrosion involves the destructive attack of metal by chemical or electrochemical reaction with its environment. Usually corrosion consists of a set of redox reactions that are electrochemically in nature. The metal is oxidized to corrosion products at anodic sites:



and hydrogen is reduced at the cathodic sites,



Because of the electrochemical nature of most corrosion processes, electrochemical methods are useful tools for studying corrosion (1-5). More specifically, electrochemical techniques can be used to measure the kinetics of electrochemical processes (e.g., corrosion rates) in specific environment and also to measure and control the oxidizing

power of the environment. The current potential relationship of a mixed-couple system is shown in Figure (3.1). The equilibrium potentials of the couples in Equations (1) and (2) are labeled $E_{eq,M}$ and E_{eq,H_2} , respectively. The corrosion potential is the potential at which the rate of oxidation of M (defined by current $i_{o,M}$) is equal to the rate of reduction of H^+ (defined by current $i_{R,H}$). Stern (6,7) has provided a firm theoretical background for determination of corrosion rates for a mixed electrode system consisting of two electrochemical reactions:

$$i_{meas} = i_{o,M} - i_{R,H} = 0 \quad \text{at } E_{corr.} \quad (3)$$

and

$$i_{corr} = i_{o,M} = i_{R,H} \quad (4)$$

$$\eta = \beta \log(i_{o,M} / i_{corr}) \quad (5)$$

$$\eta = \alpha \log(i_{R,H} / i_{corr}) \quad (6)$$

Since

$$\eta = E_{app} - E_{corr} \quad (7)$$

$$\log(i_{o,M} / i_{corr}) = \eta / \beta \quad (8)$$

$$\log(i_{R,H} / i_{corr}) = -\eta / \alpha \quad (9)$$

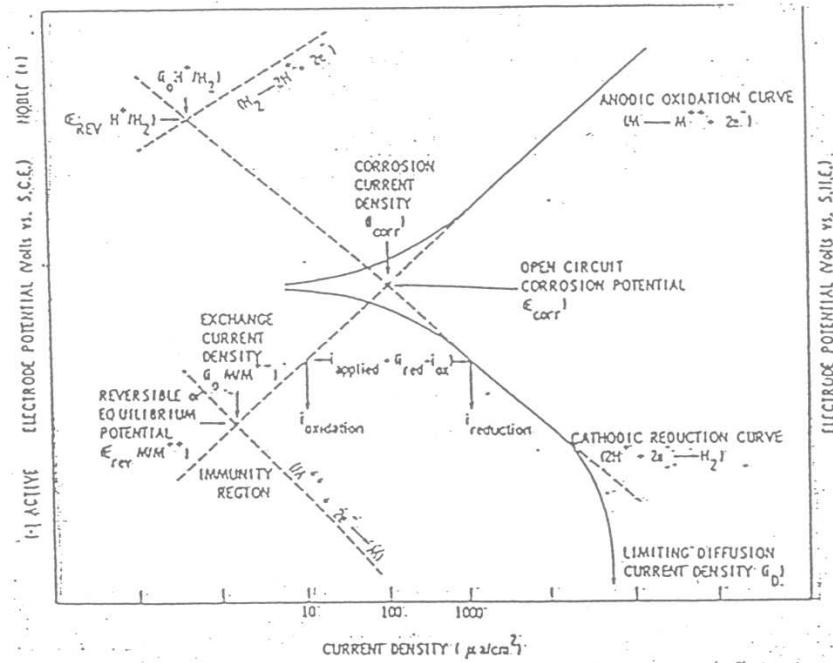


Figure (3.1): “E vs I” for mixed electrode system.

$$10^{\eta/\beta} = i_{o,M} / i_{corr} \quad (10)$$

$$10^{-\eta/\alpha} = i_{R,H} / i_{corr} \quad (11)$$

$$i_{meas} = i_{corr} (10^{\eta/b} - 10^{-\eta/\alpha}) \quad (12)$$

Since

$$10^x = 1 + 2.3x + [(2.3x)^2 / 2!] + \dots + [(2.3x)^n / n!] \quad (13)$$

$$10^{\eta/\beta} = 1 + 2.3\eta/\beta \quad (14)$$

$$10^{-\eta/\alpha} = 1 - 2.3\eta/\alpha \quad (15)$$

$$i_{meas} = 2.3i_{corr} \eta \frac{\alpha + \beta}{\alpha\beta} \quad (16)$$

$$\eta / i_{meas} = \frac{\alpha\beta}{2.3i_{corr}(\alpha + \beta)} \quad (17)$$

$$i_{corr} = \frac{\alpha\beta}{2.3(\alpha + \beta)} \frac{\Delta i}{\Delta E} \quad (18)$$

$$i_{corr} = \frac{\alpha\beta}{2.3(\alpha + \beta)} \frac{1}{R_p} \quad (19)$$

where $\Delta E/\Delta i$ = slope of the polarization curve = Polarization Resistance = R_p .

α and β = Cathodic and Anodic Tafel constants.

3.1 Calculation of Corrosion rate from the Corrosion Current.

According to Faraday's Law:

$$Q = \frac{nFW}{M} \quad (20)$$

where

Q = charge passed (coulombs).

N = number of electrons involved in the electrochemical reaction.

W = weight of electroactive species (gr).

M = Molecular weight (gr).

$$W = QM / nF \quad (21)$$

or

$$W = \frac{QxE.W.}{F} \quad (22)$$

$$W = \frac{it(EW)}{F} \quad (23)$$

W/t = CORROSION RATE, [C.R.] (g/s).

$$C.R. (cm/s) = i(E.W.) / dFA \quad (24)$$

$$C.R. (mpy) = \frac{i(EW) \times 31.6 \times 6 \times 10^6 \times 10^3}{dFA \times 2.5 \times 10^6} \quad (25)$$

$$C.R. (mpy) = \frac{0.13I_{corr}(E.W.)}{d} \quad (26)$$

where

mpy = milli-inches per year

I_{corr} =corrosion current density ($\mu A/cm^2$)

E.W=equivalent weight of the corroding species, (g).

d = density of the corroding species, (g/cm^3).

3.2 Mixed Electrodes

The utilization of the mixed-potential theory can be best demonstrated by considering mixed electrodes. A mixed electrode is metal sample that is in contact with two or more oxidation-reduction systems. For example, in the case when zinc is immersed in hydrochloric acid, this metal is rapidly corroded and the electrochemical reactions occurring are shown in Figure (3.2)

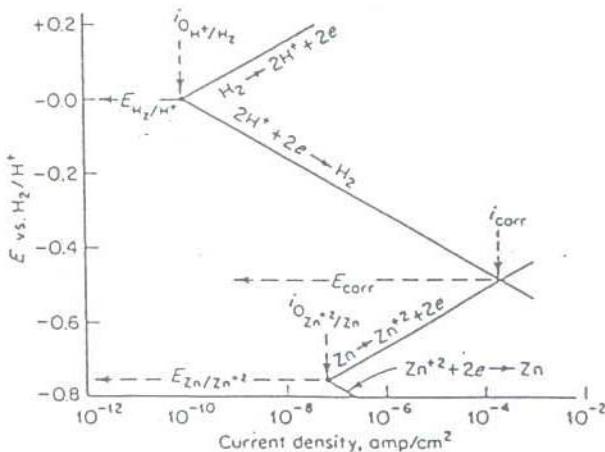


Figure (3.2) "E vs i" for Zn in acid solution.

If we consider a zinc electrode in equilibrium with its ions, it would be represented by a reversible potential corresponding to the zinc-zinc-ion electrode reaction, and a corresponding exchange current density. However, if we consider the hydrogen-electrode reaction occurring on a zinc surface under equilibrium conditions, then this state would be represented by the reversible potential of the hydrogen electrode and the corresponding exchange current density for this reaction on a zinc metal ions, the electrode cannot remain at either of these two reversible potentials. This new potential is achieved when the second hypothesis of the mixed-potential theory is satisfied; that is,

the total rate of oxidation must be equal the total rate of reduction. The only point in this system where the total rates of oxidation and reduction are equal is at the intersection represented by a "mixed" or corrosion potential E_{corr} . At this point the rate of zinc dissolution is equal to the rate of hydrogen evolution expressed in terms of current density.

To illustrate the importance is kinetic factors in determining the corrosion behavior of a metal let us examine the corrosion behavior of iron on dilute hydrochloride acid solution. As shown in Figure (3.3), besides the fact that the free energy for the dissolution of iron is lower than that of pure zinc due to the very low exchange current density for the hydrogen reaction on zinc surfaces.

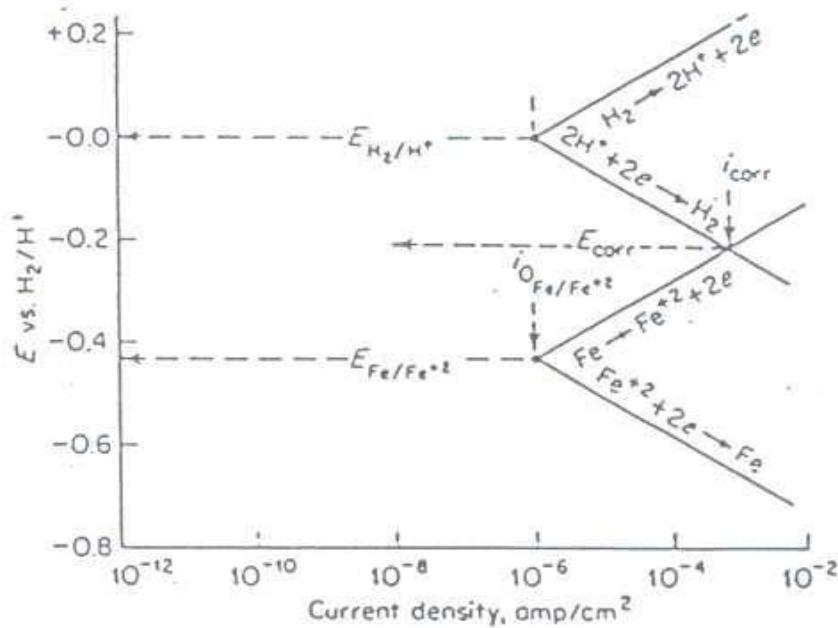


Figure (3.3) "E vs i" for Fe in acid solution.

In Figure (3.4) is represented a system where the reduction process is under diffusion control. In this case, the metal follows the typical anodic dissolution reaction under activation control.

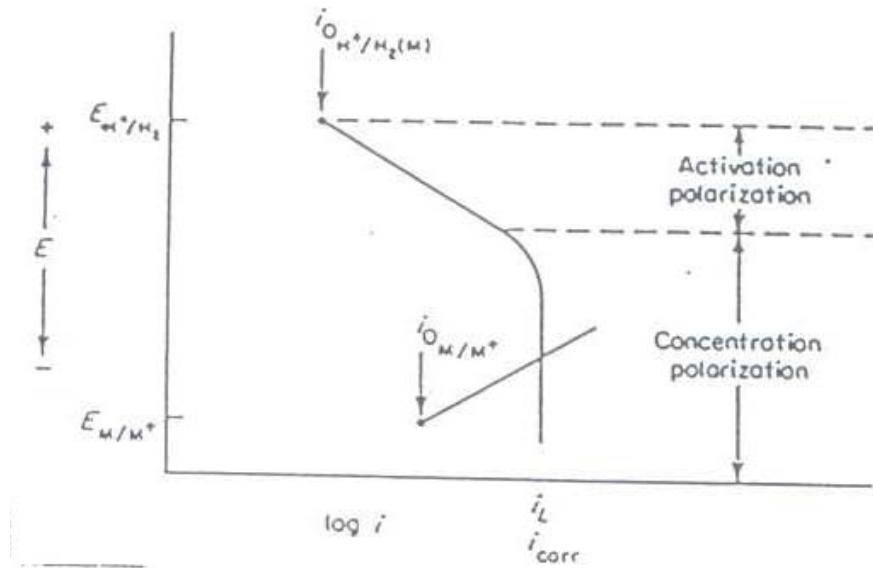


Figure (3.4) Corrosion of metal M under diffusion control.

The reduction process follows the equation:

$$\eta_{red} = -\alpha \log \frac{i_c}{i_o} + 2.3 \frac{RT}{nF} \log \left(1 - \frac{i_c}{i_l} \right) \quad (27)$$

where,

$$i_l = \frac{DnFC}{x} \quad (28)$$

i_l = limiting diffusion current density A/cm².

D = diffusion coefficients cm²/s.

C = concentration of the reacting ions on the bulk solution moles/cm³.

X = the thickness of the diffusion layer cm.

Initially, in Figure (3.4) the reduction rate of hydrogen ions is under activation control; at higher reduction current it is controlled by concentration polarization. The corrosion rate of this system is equal to i_{corr} of i_l and is determined by the intersection between the total reduction rate and the total oxidation rate.

3.3 CORROSION RATE MEASUREMENTS

Linear Polarization Technique Within 10 mV more noble or more active than the corrosion potential, it is observed that the applied current density is linear function of the electrode potential. This is illustrated in Figure (3.5) and Figure (3.6).

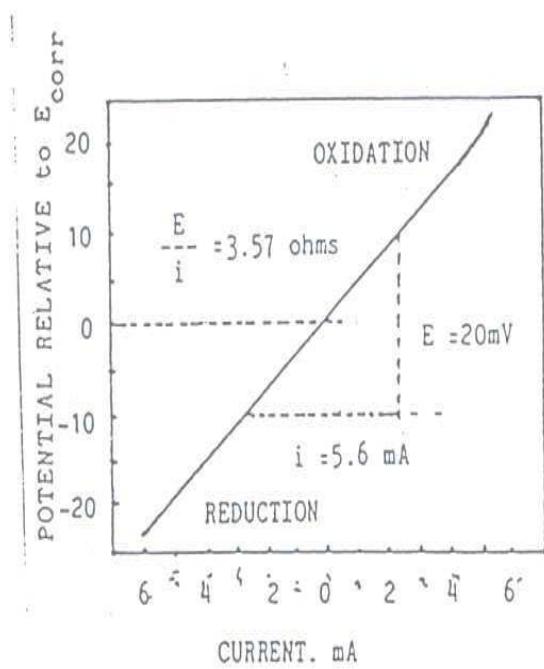


Figure (3.5) Experimentally Measured polarization resistance.

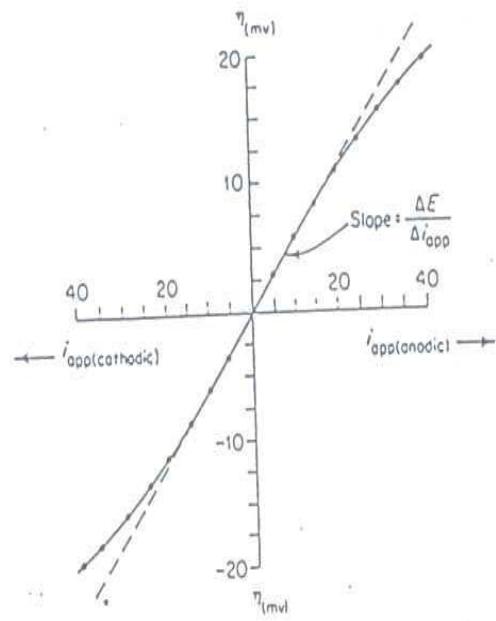


Figure (3.6) Applied-current linear-polarization curve.

In Figure (3.6), the corrosion potential is used as an overvoltage reference point and a plot of overvoltage *vs* applied anodic and cathodic current is shown on

a linear scale. This plot represents the first 20-mV polarization of the applied current cathodic polarization curve shown in Figure (3.7). The slope of a linear-polarization curve is controlled mainly by i_{corr} and is insensitive to changes in α and β values as shown in Equation (19). Assuming the $a=b=120\text{mV}$ represent the average of all corrosion systems, Equation (19) reduces to (6,7):

$$i_{corr} = \frac{0.026}{R_p} \quad (29)$$

Equation (29) may be used to calculate the corrosion rate of a system without knowledge of its electrode-kinetic parameters. Although the accuracy of this approximation may not always be sufficient, Equation (29) provides a unique basis for rapidly measuring relative corrosion rates or changes in corrosion rate.

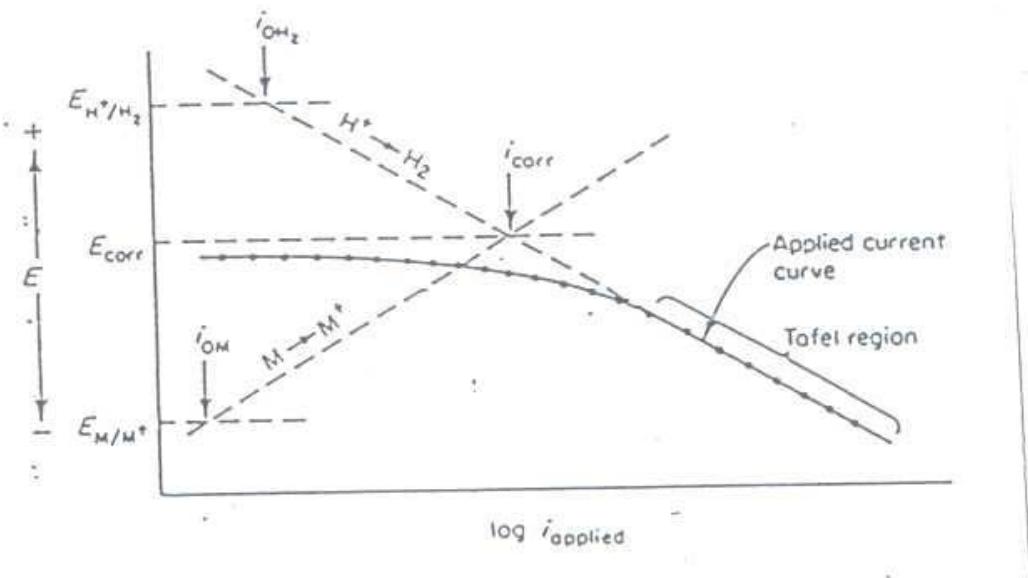


Figure (3.7) Tafel Extrapolation Method.

This technique offers the following significant advantages:

1. The polarization resistance method measures the instantaneous corrosion rates as compared to other methods on which metal loss is measured over a finite period of time. Instantaneous means that each reading on the instrument can be translated directly into corrosion rate.
2. The experiment can be completed in a matter of minutes and the small polarization from the corrosion potential do not disturb the system. This permits rapid rate measurements and can be used to monitor corrosion rate in various process streams.
3. This technique may be used for accurately measuring very low corrosion rates (less than 0.1 mpy). The measurements of low corrosion rates are especially important in food processing industries where trace impurities and contamination are problems.
4. Electrochemical corrosion rate measurements may be used to measure the corrosion rate of structures that cannot be visually inspected or subjected to weight loss tests.

3.4 Tafel Extrapolation Method

This technique uses data obtained from cathodic and anodic polarization measurements. Cathodic data are preferred, since these are easier to measure experimentally. In Figure (5.7) the total anodic and cathodic polarization curves corresponding to hydrogen evolution and metal dissolution are superimposed as dotted lines. It can be seen that at relatively high-applied current densities the applied current density and that corresponding to hydrogen evolution have become virtually identical. To determine the corrosion rate from such polarization measurements, the Tafel region is extrapolated to the corrosion potential, as shown in Figure (5.8).

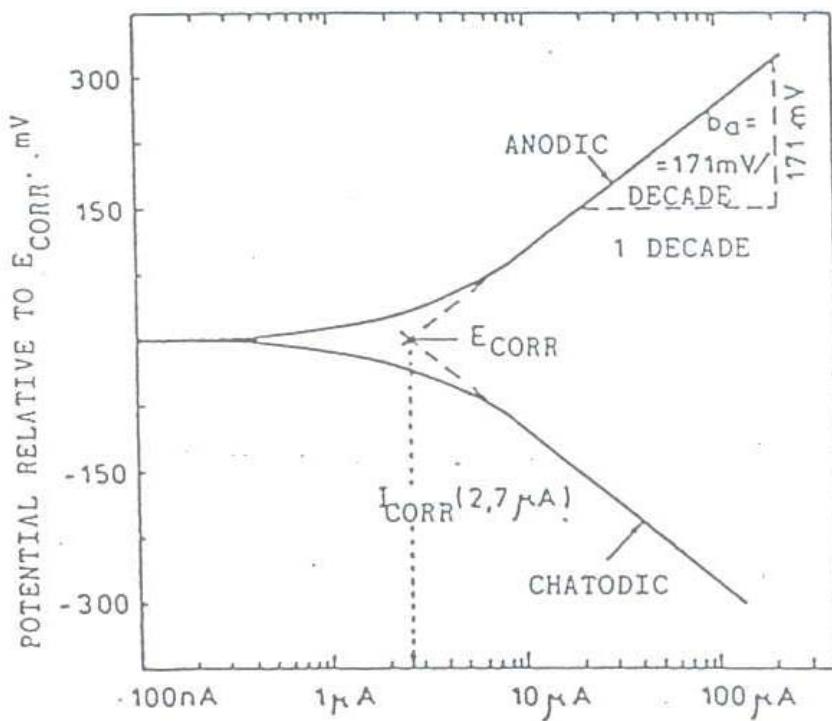


Figure (3.8) Corrosion rate determination.

At the corrosion potential, the rate of hydrogen evolution is equal to the rate of metal dissolution, and this point corresponds to the corrosion rate of the system expressed in terms of current density. Tafel constants must be calculated from both the anodic and cathodic portions of the Tafel Plot. The units of the Tafel constants is V/decade. A decade of current is one order of magnitude. A Tafel constant calculation is illustrated in Figure (3.8). These measurements may be complicated by two interfering phenomena: concentration polarization and resistance drop effects (8,9).

Concentration polarization occurs when the reaction rate is so high that the electroactive species cannot reach the electrode surface at a sufficient rapid rate and the reaction rate becomes diffusion controlled.

Resistance drops across the solution can also cause nonlinear Tafel behavior at high currents:

$$E_{IR} = i_{meas} R_{sol} \quad (30)$$

This method offers the following significant advantages:

1. Under ideal conditions, the accuracy of the Tafel extrapolation method is equal or greater than conventional weight loss methods.
2. With this technique it is possible to measure extremely low corrosion rates, and it can be used for continuous monitoring the corrosion rate of a system.
3. Tafel Plots can provide a direct measure of the corrosion current, which can be related to corrosion rate.
4. The rapid determination of corrosion rates with Tafel Plots can be advantageous for such studies as inhibitors evaluation and alloy comparisons.

3.5 Potentiodynamic Polarization Measurements.

The potentiodynamic polarization technique is generally used to produce a qualitative picture or “fingerprint” of a substance in a given solution [see Figure (4.9)]. It also detects important information such as:

1. The potential region over which the specimen remains passive.
2. The corrosion rate in the passive region.
3. The ability of the material to spontaneously passivate in the particular medium.

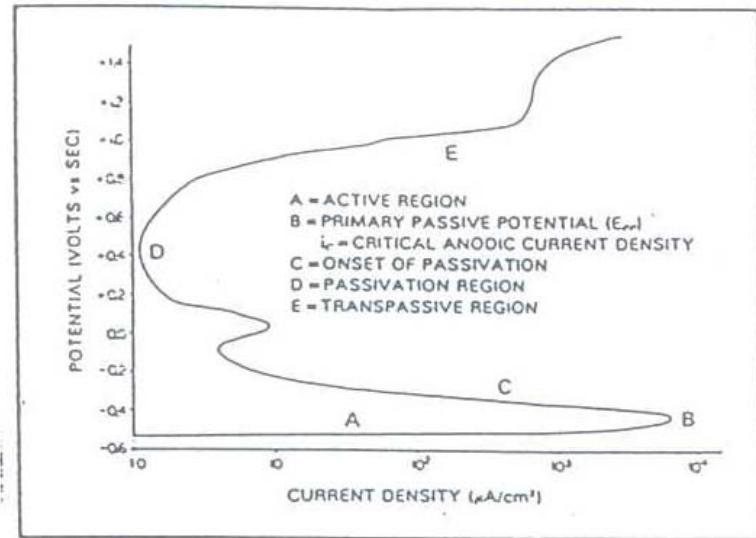


Figure (3.9) Standard potentiodynamic anodic polarization plot of 430 Stainless Steel.

Region “A” in Figure (3.9) is the region in which the metal specimen corrodes, as the applied potential is made more positive. At “B” the onset of passivation begins. The passivation begins. The passivation is probable due to the formation of a film on the surface of the metal. This point is characterized by two values, the primary passive potential (E_{pp}) and the critical current density (i_c). In region C, the current decreases rapidly as the passivating film forms on the specimen. The passivating film begins to break down in the region E, the transpassive region where oxygen evolution starts to occur.

When the anodic current is interrupted, passivity decays within a short time in the manner shown by Figure (3.10). The potential first changes quickly to a value still noble on the hydrogen scale, then changes slowly for a matter of seconds to several minutes. Finally, it decays rapidly to the normal active value was found by Flade (10) to be more noble the more acid the solution on which passivity decayed. This characteristic potential

was later called the Flade potential and Franck (11) found that it was a linear function of pH. His measurements, combined with later data by others, provide the relation at 25°C:

$$E_F = -0.63 + 0.059 pH \quad (31)$$

This reproducible Flade potential and its 0.059-pH dependence is characteristic of the passive film on iron.

Stability of passivity is related to the Flade potential, assuming the following schematic reaction to take place during anodic passivation:



the oxidation potential for which is E_F , and OM refers to oxygen in the passive film on metal M whatever the passive film composition and structure may be. The amount of oxygen assumed to be combined with M has no effect on present consideration. It follows, as observed, that

$$E_F = E_F^o - \frac{0.059}{2} \log(H^+)^2 = E_F^o + 0.059 pH \quad (33)$$

The negative value of E_F^o for iron (-0.63-V) indicates considerable tendency for the passive film to decay-reverse reaction (32)-whereas an observed positive value of $E_F^o=0.2$ V for chromium indicates conditions more favorable to passive film formation and greater stability of passivity.

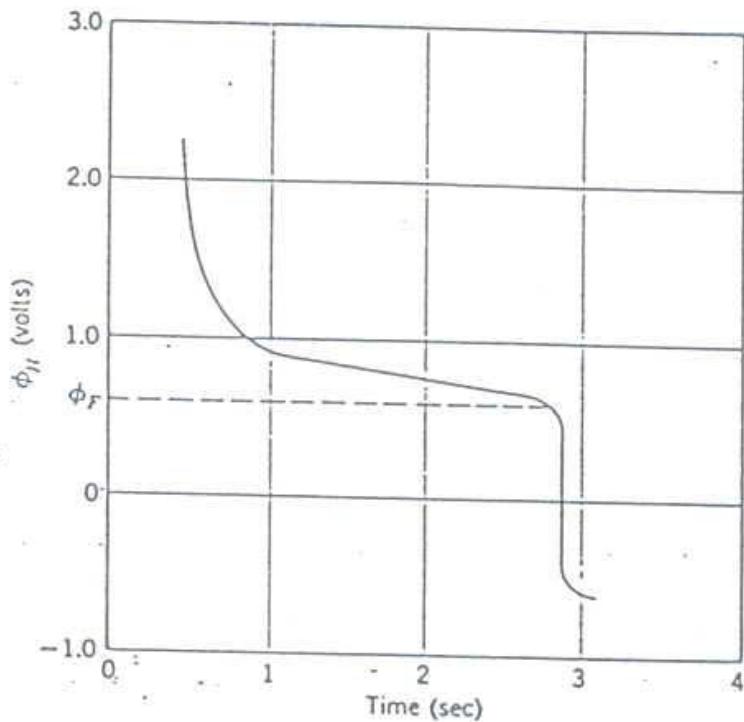


Figure (3.10) Decay of passivity of iron on 1 N H_2SO_4 showing Flade potential.

In Figure (3.11), on the anodic polarization curves are superimposed three cathodic polarization curves. Each cathodic curve represents a single reduction process with different possible exchange current densities.

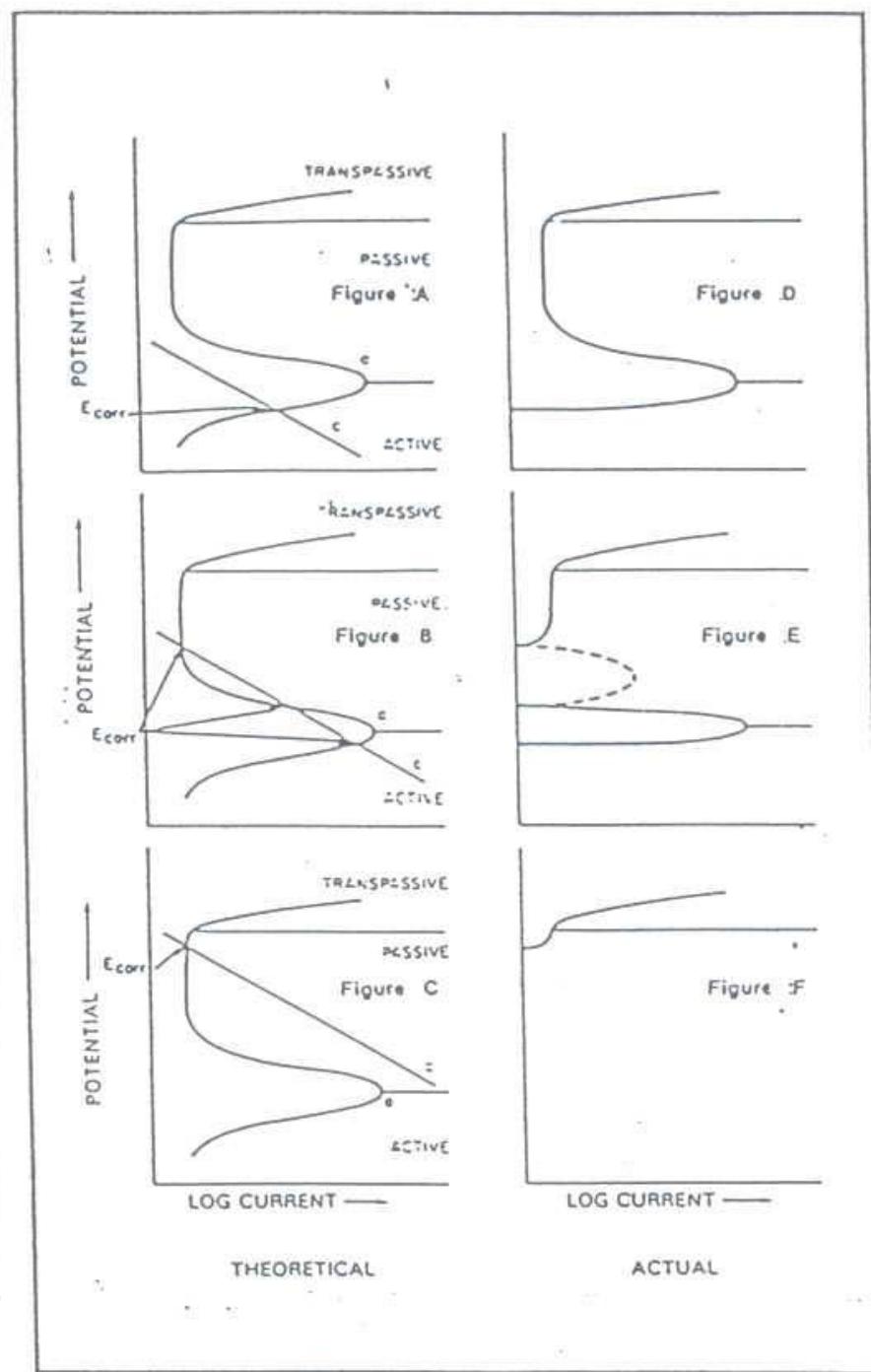


Figure (3-11) Theoretical and actual potentiodynamic polarization plots of active-passive metals.

If the cathodic intersects the anodic curve in the active region as in Figure (A), the specimen will corrode rapidly. Figure (D), the experimental counterpart to the theoretical Figure (A) shows very similar shape.

If the cathodic curve intersects the anodic curve as in Figure (B), the specimen can exhibit either high corrosion rates or low corrosion rates. Figure (B) indicates intersections in each of active, partially passive, and passive region. Figure (E) represents the experimental counterpart to the theoretical Figure (B).

If the cathodic curve intersects the anodic curve in the passive region as in Figure (C), the material will passivate spontaneously. Experimentally, Figure (F) does not exhibit the peak-shaped active to passivate transition because the specimen has already been fully passivated.

Potentiodynamic polarization measurements are valuable in rapidly identifying desirable materials-environment combinations and in predicting how a material will behave when exposed to a particular environment.

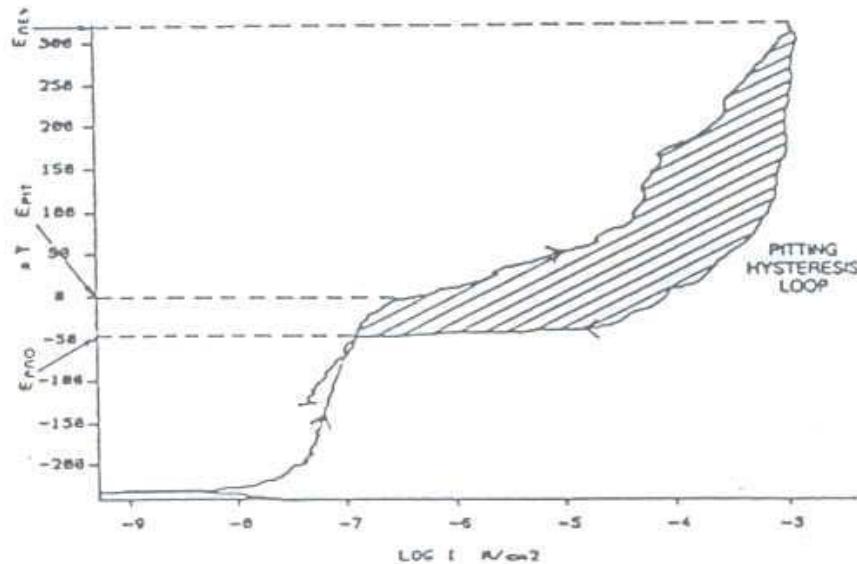


Figure (3.12) Typical cyclic polarization plot.

Cyclic Polarization This technique measures the pitting tendencies of a specimen in a given metal-solution system. In a pitting experiment, one applies a potential scan beginning at E_{corr} in the anodic direction until a large increase on current occurs. The threshold current density is typically 1mA/cm^2 . The final potential of the scan should be negative with respect to E_{PRO} as determined by a preliminary scan. The potential where the loop closes on the reverse scan is the protection (or repassivation) potential (E_{PRO}). If the loop does not close, E_{PRO} can be estimated by extrapolating the reverse scan to zero current. The potential at which the current sharply increases is defined as the pitting potential (E_{PIT}) as shown in Figure (3.12). If the pitting potential and the protection potential are the same, there will be little tendency to pit. If the protection potential is more positive (anodic) than the pitting potential, there will be no tendency to pit.

If the protection potential is more negative than the pitting potential, pitting could occur. The size of the pitting loop is rough indication of pitting tendency; the larger the loop, the greater the tendency to pit (12-14).

EXPERIMENTAL PROCEDURE

REQUIRED EQUIPMENT AND SUPPLIES

HY-130 steel

INCONEL-718

0.1 M H_2SO_4

0.5 M KOH

PAR Model 352 Corrosion System

PAR Corrosion Cell

PROCEDURE

Objective:

1. **CORROSION RATES:** The Experiments will include Polarization Resistance Measurements, Potentiodynamic Polarization Measurements, Tafel Extrapolation Method, and Cyclic Polarization with subsequent calculations of the rates for INCONEL-718 in 0.1 M H_2SO_4 and for HY-130 steel in 5 M KOH.

Conduct linear polarization measurements, potentiodynamic polarization measurements, cyclic polarization measurements and obtain Tafel curves as suggested previously for INCONEL-718 in 0.1 M H_2SO_4 and for HY-130 steel in 5 M KOH.

The electrochemical cell [see Figure (3.13)] employed for these studies should be a conventional three compartment and the reference electrode via a Luggin probe. The polarization experiments should be carried out using standard calomel electrode (SCE) and Hg/HgO reference electrode in 0.1 M H_2SO_4 and in 5 M KOH, respectively.

Calculation Procedure

- A. Obtain Linear Polarization Plot, Tafel Plot, Potentiodynamic Polarization Plot and Cyclic Polarization Plot for INCONEL-718 in 0.1 M H₂SO₄.
1. Compute the corrosion rate in (myp) and in (cm/s) using linear polarization method and Tafel extrapolate method. For more accurate results, the Tafel constants must be independently determined from a Tafel plot and substituted in Equation (19). Also, verify that the value 0.026 from Equation (29) was derived and discuss the units of the equation. Compare the corrosion rate obtained by linear polarization method with the rate obtained using Tafel extrapolation method.
2. Compare the anodic ($d\eta/d\log i$) for both alloys.
3. Compute the transfer number β .
4. Compute the Cathodic ($d\eta/d\log i$).
5. Compute the transfer number α .
6. Compute the potential over which the specimen remains constant.
7. Compute the corrosion rate in the passive region.
8. Compute the ability of the material to spontaneously passivate in the particular medium.
9. Compute the protection or repassivation potential E_{PRO} from cyclic polarization curves.
10. Compute the pitting potential (E_{PIT}).
11. Determine the pitting tendency of INCONEL-718 in sulfuric acid.

B. Obtain Linear Polarization Plot, Tafel Plot, Potentiodynamic Polarization Plot and Cyclic Polarization Plot for HY-130 in 5 M KOH.

1. Compute the corrosion rate in (myp) and in (cm/s) using linear polarization method and Tafel extrapolation method. For more accurate results, the Tafel constants must be independently determined from the Tafel plot and substituted in your experiments. Show how Equation (29) was derived and discuss the units of the equation. Compare the corrosion rate obtained by linear polarization method with the rate obtained using Tafel extrapolation method.
2. Compute the anodic ($d\eta/d\log i$).
3. Compute the transfer number β .
4. Compute the cathodic ($d\eta/d\log i$).
5. Compute the transfer number α .
6. Compute the potential over which the specimen remains constant.
7. Compute the corrosion rate in the passive region.
8. Compute the ability of the material to spontaneously passivate in the particular medium.
9. Compute the protection or repassivation potential E_{PRO} from cyclic polarization curves.
10. Compute the pitting potential (E_{PIT}).
11. Determine the pitting tendency of HY-130 in 5 M KOH.

2. CALCULATION OF STANDARD FLADE POTENTIAL

A. Calculate the Standard Flade Potential at 25°C for iron assuming that the passive film substance represented schematically as OM in Equation (32) is Fe_2O_3 .

Data: ΔG° of formation for Fe_2O_3 =-741 kJ; for $\text{H}_2\text{O(l)}$ =-273 kJ.

B. On breakdown of passivity, a corrosion current density of 0.05 A/cm^2 occurs for one second on iron in accord with $2\text{Fe} + 3/2 \text{ O}_2 \rightarrow \text{Fe}_2\text{O}_3$. Calculate the thickness of Fe_2O_3 layer formed (based on apparent area of 1 cm^2). [$M_{\text{Fe}_2\text{O}_3}=159.7$]; $d=5.12 \text{ g/cm}^3$.

3. RATE OF CORROSION OF METAL IN WATER

Using Tafel Equation derive.

A. Corrosion potential equation [Dependence of E_{corr} vs i_o^{H} and i_o^{M}].
B. Corrosion current equation.

4. CONSTRUCTION OF “E-logi” DIAGRAM FOR THE CORROSION OF IRON ON HYDROGEN-SATURATED SOLUTION

Contract and E-logi diagram for the corrosion of iron on hydrogen-saturated oxygen-free solution of $\text{pH}=3.5$ and $a_{\text{Fe}}=0.05$ (molar scale).

For iron dissolution, $i_o = 8.5 \times 10^{-7} \text{ A cm}^{-2}$; anodic $d\eta/d(\log i)=0.04 \text{ V}$; and $E^\circ_{\text{Fe/Fe}^{+2}}=-0.44 \text{ V}$. For the hydrogen evolution reaction (h.e.r.), the cathodic $d\eta/d(\log i)=-0.100 \text{ V}$ and $i_o=3.0 \times 10^{-6}$. Calculate the cathodic protection current required to reduce the corrosion rate to zero (i.e., less than 10^{-6} A/cm^2).

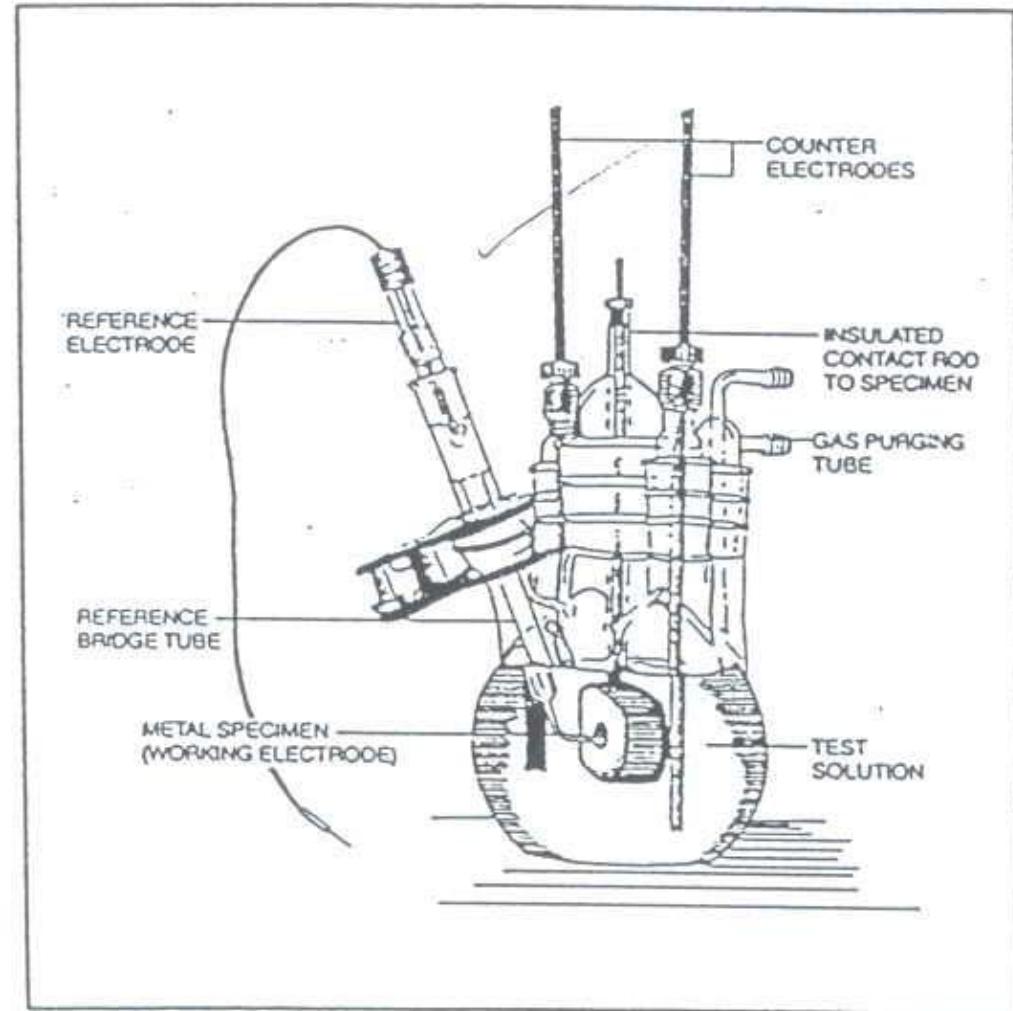


Figure (3.13) A typical electrochemical corrosion test cell.

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